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by P. P./Schmidt

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far infrared-active vibrations of the caged ions are known.
With the use of the equilibrium condition for the cage of solvent,
the values of the parameters can be determined. Although all
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of independent R^{-6} and R^{-12} terms together with other
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for the alkali metal cations.

Potential Energy Functions for the Solvation of
Alkali Metal Cations

by

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Abstract

The purpose of this paper is to explore the use of several model potential energy functions in order to try better to understand the nature of the forces which operate between simple monatomic cations and the molecules of solvent which surround them. This work builds upon and extends a recently reported initial treatment. In that report, the potential energy was modelled as the sum of an exponential (Born-type) repulsion and an ionic-dipolar attraction. In this paper we consider composite functions which consist variously of an exponential form of repulsion or an inverse R-12 repulsion, and attractions which are expressed in terms of the basic ionic-dipolar terms together with additional terms which depend upon the polarizabilities of the ion and the solvent. No more than two adjustable parameters are used. The force constants for the far infrared-active vibrations of the caged ions are known. With the use of the equilibrium condition for the cage of solvent, the values of the parameters can be determined. Although all of the functions examined show the effect of the polarizability of the ion on the force constants, a potential which consists of independent R^{-6} and R^{-12} terms together with other experimentally fixed ionic-dipolar terms shows most clearly the effect of polarizability. We also find, however, that the consideration of ionic polarizability alone is inadequate to explain in a simple manner the variation of the force constants for the alkali metal cations.

1. Introduction

It is generally assumed that for most cations in solution, and even for those for which no effective covalently bonded associations form, a discrete and persistent structure of solvent molecules accompany a centrally located ion. One can propose significant, discrete structures which may contribute to chemical reactivity or transport processes which take place in solution. Thus, for a variety of reasons there is a need to try to understand the nature of the forces which bind solvent to ion in such an impermanent environment as that of a solution.

It is the purpose of this paper to present several forms of potential energy function for the simple solvated alkali metal cation. An ultimate objective of this kind of investigation should be to specify an accurate form of the function. No claim is even hinted that we are anywhere near that goal. On the contrary, here only short-ranged, intermediate--but necessary--objectives are set. Specifically, we fit parameters in these model potential functions with available spectroscopic data. At this stage it is necessary to see if it is possible to choose one form rather than another as being more "accurate" with respect to physical interpretation. As we amply illustrate in this paper, the stage has not been reached where it is possible to assay the numerical accuracy of any particular form of potential energy function. For that assay, different experiments with new sets of data are required.

As we indicated in a recent paper,[1] the solvated alkali metal

cations are ideal subjects to study because of the relatively
uncomplicated nature of the electronic structure of the centrally
located ions. Thus, one suspects, the predominant forces of inter-
action are electrostatic with strong repulsions entering only
on very close approach between the ion and its solvent. The
process of modelling the appropriate potential energy function is
thereby simplified. Experimental evidence in the form of the
far infrared-active vibrations of the alkali cations[2] definitely
suggests that the ions occupy some form of cage of solvent and that
the cage endures for a sufficient length of time for the vibrations
to be observed.

In the previous paper,[1] we modelled the interactions between
the centrally located ion in a cage of solvent and the molecules
of solvent which make up the cage as the simple sum of an ion-dipole
interaction and an exponential, Born-type repulsion. An equilibrium
condition for the single ion-solvent couple was used to fix values
for the adjustable parameters in the Born repulsion. Most importantly,
we showed that because the ion oscillates about a position of
equilibrium which also is the centre of symmetry, the force constant
does not depend directly upon any electrostatic ionic-dipolar terms.
The contribution of the electrostatic interaction between the ion and
a regular, crystalline cage of dipoles vanishes for the force
constant by reasons of symmetry. The form of the force constant
which we obtained indicated a direct dependence on the forces of
repulsion which operate.

We also showed in the previous paper[1] that the force constants
for the vibrations of the alkali cations in their cages of solvent
range from a high value for lithium to a low value for potassium.

However, from potassium to caesium, the force constants again increase. We indicated that this effect could be attributed to the increasing polarizability of the electrons in the ions as the group is transcended from lithium to caesium. Our arguments in that preliminary report,[1] however, were only qualitative. An aim of this paper is to attempt to make the dependence of the force constant on the polarizability of an ion explicit and quantitative. We want to see if the trend in the force constants for the group of the alkali metal cations follows the trend in the increase in the observed polarizabilities.

We consider the following potential energy functions. First, we re-examine the composite function which consists in part of the Born exponential type of repulsion. Several years ago, Woodcock[3] considered a generalized form of exponential-type of repulsion in connection with a study of the alkali halide solids. A Woodcock-form of repulsion is used in the second example function. An advantage of the Woodcock generalized repulsion is the fact that the "hardness" of the repulsion can be adjusted easily. Finally, we consider composite functions which are constructed of Lennard-Jones and Mie (or decoupled Lennard-Jones) potentials. We will demonstrate that the use of the Lennard-Jones potential in a Stockmayer-form of potential leads to pathological conditions. In particular, one is not free to choose values of the radii of solvation for the ions at will. The use of the Mie potential, on the other hand, shows a remarkable R^{-6} repulsion for the interaction of the ion with the solvent both for lithium and sodium.

Before we present the analyses of the various potential forms in detail, it is necessary to consider some procedural and mathematical

preliminary operations. These operations are outlined in the next section.

2. Method of approach

In this paper we consider the same systems as we considered previously,[1] viz., the solvated alkali metal cations. As indicated above, here we consider more complicated, and one presumes, more realistic, potential energy functions. These potential energy functions are constructed as the sums of terms: repulsions and attractions. In particular, we consider various ionic-dipolar attractions, dipolar repulsions between molecules of solvent in the first shell of solvation, dipolar-induced dipolar attractions between solvent molecules and between the solvent and the ion, and finally in some cases, induced dipole-dipolar interactions between the ion and the solvent. In all cases, the polarizability of the solvent, as found with the use of the Lorenz-Lorentz[4] equation, is used. In some of the cases, the polarizability of the ion is used; the values are those given in Smyth's book.[5] The parameters which are adjustable and require fitting to ex perimental data are contained in the exponential repulsions or the Lennard-Jones (or Mie) components. Throughout, we allow for only two adjustable parameters. These two parameters can be fitted to values of the force constants for the far infrared-active vibrations of the ion. The expression for the force constant and the condition for equilibrium yield two expressions to use to solve for the two parameters.

For the solvated ionic systems, there are only limited un-

ambiguous experimental data available which can be used to determine
the parameters in any model potential energy functions. Indeed,
as long as the question of the coordination number of the solvent
about any one of the alkali metal cations remains open, there are
no data which are certain. We assume in this paper that the
coordination number of solvent for lithium, sodium, and potassium
is four. The coordination number of solvent for rubidium and caesium
is most likely to be six. It is then possible to establish the
values for the force constants for the far infrared-active vibrations
of these ions.[1]

Data which are used in the following section to establish
values of the adjustable parameters within each model potential
energy function are given in Table 1. The values of the radii
of solvation are those used previously[1] and are found with the
use of the Stearn-Eyring[6] model as applied by Abraham and Liszi.[7]
The polarizability of the solvent (taken to be dimethyl sulphoxide,
DMSO) is found with the use of the Lorenz-Lorentz[4] equation

$$\frac{n^2-1}{n^2+2} V_m = 4\pi\alpha/3 \qquad (2.1)$$

in which n is the index of refraction, V_m is the molar volume, and
α is the polarizability.

a. Formulae for the force constant

As we showed in the previous paper,[1] when considering the far
infrared-active vibrations of a solvated ion, it is essential to
develop expressions for the force constants in an appropriate form.
The vibrations are known experimentally[2] to involve the oscillation
of the ion about a position of equilibrium at the centre of a
cage of solvent. We assume the cage is regular and crystalline.
Thus, the position of equilibrium is also the centre of symmetry.
It is necessary, therefore, to obtain the force constant as the
second order coefficient in a Taylor series expansion about the
centre of symmetry.

For the electrostatic interaction between the ion and its
solvent dipoles, the Carlson-Rushbrooke[8] expansion can be used. For
cages of solvent which are distributed about the ion with cubic
symmetry, these electrostatic terms do not contribute to the magnitude
of the force constant. For other potential functions an integral form
of the Taylor series has proved useful. This form was presented
to second order in the previous paper.[1] Recently, we have generalized
the result to any order.[9,10] The essential formulae are listed below.

Frequently, one encounters potential energy functions which
do not easily yield Fourier transforms. The need for the Fourier
transform of a function is essential in evaluating the integral
form of the force constant--see below. When the Fourier transform
cannot be found, yet the function is otherwise well-behaved,
it is necessary to revert to a differential form. Therefore, we
also present below a differential form which is useful in evaluating

the force constant associated with the Wookcock generalized exponential form.

The force constant for the vibration of an ion about its equilibrium position at the centre of a cage of solvent is obtained as follows. The formula for the second order contribution to the Taylor series is[1,9]

$$\frac{1}{2}(\underset{\sim}{r}\cdot\underset{\sim}{\nabla}_R)^2 G(\underset{\sim}{R}) = \frac{1}{2} r^2 \sqrt{4\pi} \sum_\ell (-i)^{\ell+2} A_{2\ell} P_\ell(\hat{r}\cdot\hat{R}) I_{2\ell}(R) \tag{2.2}$$

where

$$I_{2\ell}(R) = \frac{1}{(2\pi)^3}\int_0^\infty dk \ k^4 f(k) j_\ell(kR) \tag{2.3}$$

and $j_n(x)$ is the spherical Bessel function of the first kind.[11] In eqn (2.2) $P_n(x)$ is the Legendre polynomial.[11] The argument $\hat{r}\cdot\hat{R}$ of the Legendre polynomial is the scalar product of the unit vectors $\hat{r}$ and $\hat{R}$. The vector $\underset{\sim}{R}$ is directed from the molecule of solvent to the centre of symmetry and the vector $\underset{\sim}{r}$ expresses an excursion away from that point. The function $f(k)$ is defined by[1,9]

$$f(k) = (4\pi)^{3/2}\int_0^\infty dr \ r^2 G(r) j_0(kr) \tag{2.4}$$

when $G(r)$ is a scalar function. The coefficient $A_{2\ell}$ has two values 1/3 and 2/3 according as $\ell = 0$ or 2.

For a system of solvation which is regular and crystalline in either a tetrahedral or octahedral sense, it is easily shown that the the $\ell = 2$ terms vanish when summed over the sources.

Thus, the contribution to the force constant from an individual term in the potential, $G(r)$, is

$$^c k = - c\sqrt{4\pi}\, I_{20}(R_0)$$

$$= - \frac{c}{4\pi^{5/2}} \int_0^\infty dk\; k^4 f(k) j_0(kR_0) \tag{2.5}$$

where c is the coordination number for the cage of solvent.

If the function $G(r)$ is the exponential Born repulsion

$$\phi_{exp} = B\, \exp[-(R-R_0)/\rho] \tag{2.6}$$

then this **term** will contribute

$$^c k_{exp} = \frac{cB}{3\rho^2}(1 - 2\rho/R_0) \tag{2.7}$$

to the total force constant.[1] On the other hand, for a term in the potential of the form R^{-m}, a contribution of the form

$$^c k_m = \frac{m(m-1)}{3R_0^{m+2}} \tag{2.8}$$

is found.[9]

Equation (2.4) defines the radial component of the Fourier transform of a function $G(r)$. As indicated, frequently one encounters well-behaved functions which nevertheless fail to yield easily analytical expressions for $f(k)$. In some instances, although it is possible to find an analytical form for $f(k)$, it is not possible

easily to find the integral (2.3). On the other hand, such functions may yield readily to differential operators. One function which satisfies this classification is the Woodcock generalized exponential repulsion[3a]

$$\phi_W(R) = BR^{-m}\exp[-(R^n - R_0^r)/\rho^n].$$ (2.9)

We now develop the differential form for the force constant term (2.5). The complete expression for the second order term in the Taylor series is given as[1,9]

$$t_2(r,R) = \sqrt{4\pi}\,\frac{r^2}{2}\left[-\frac{1}{3}I_{20}(R) + \frac{2}{3}P_2(\hat{r}\cdot\hat{R})I_{22}(R)\right]$$ (2.10)

for a function

$$G(\underset{\sim}{r}) = \sqrt{4\pi}\,Y_{00}(\hat{r})F(r)$$

(2.11)

in which $Y_{00}(\hat{r})$ is the zeroth-order spherical harmonic function. The problem is to convert $I_{20}(R)$ and $I_{22}(R)$ to differential forms.

First, for $I_{20}(R)$ we write from the definition of the integral, eqn (2.3)

$$I_{20}(R) = \frac{1}{(2\pi)^3}\int_0^\infty dk\; k^4 f(k)j_0(kR)$$

$$= -\frac{1}{(2\pi)^3}\frac{1}{R}\frac{\partial^2}{\partial R^2}R\int_0^\infty dk\; k^2 f(k)j_0(kR)$$ (2.12)

Into the integral on the second line of eqn (2.12) we substitute the definition of f(k). Changing the order of integration gives

$$\int_0^\infty dk \; k^2 f(k) j_0(kR) = (4\pi)^{3/2} \int_0^\infty dk \; k^2 j_0(kR) \int_0^\infty dr \; r^2 F(r) j_0(kr)$$

$$= \frac{4\pi^{5/2}}{R^{3/2}} \int_0^\infty dr \; r^{3/2} F(r) \delta(r-R)$$

$$= 4\pi^{5/2} F(R) \tag{2.13}$$

where $\delta(r)$ is the Dirac delta function. Substitution of this result into the equation for $I_{20}(R)$ gives

$$I_{20}(R) = - \frac{1}{\sqrt{4\pi}\; R}\left[2\; \frac{\partial F}{\partial R} + R\; \frac{\partial^2 F}{\partial R^2} \right]. \tag{2.14}$$

For the evaluation of the second term $I_{22}(R)$, we use the lowering operator for the spherical Bessel function twice:[11]

$$j_{n+1}(x) = [n/x - d/dx] j_n(x). \tag{2.15}$$

Thus, by means of an operation similar to the above to get (2.14), we find

$$I_{22}(R) = \frac{1}{\sqrt{4\pi}} \left[\frac{\partial^2}{\partial R^2} - \frac{\partial}{R\partial R} \right] F(R). \tag{2.16}$$

The collected result is

$$t_2(R) = \frac{1}{2}\; r^2 \left\{ \frac{1}{3R}\left[2\frac{\partial F}{\partial R} + R\frac{\partial^2 F}{\partial R^2} \right] + \frac{2}{3}P_2(\hat{r}\cdot\hat{R})\left[\frac{\partial^2 F}{\partial R^2} - \frac{1}{R}\frac{\partial F}{\partial R} \right] \right\}. \tag{2.17}$$

The form of (2.17) is the same as (2.10) as far as any angular dependencies are concerned. Therefore, for collections of sources which are distributed with cubic symmetry, the $P_2(\hat{r}\cdot\hat{R})$ terms vanish when summed over all the sources. The application of the result to the Woodcock generalized exponential potential, eqn (2.9), yields

$$c_{k_{W(m,n)}} = \frac{c}{5}\,\frac{B}{R_0^{m+2}}\left[m(m-1) - n(n-2m+1)(R_0/\rho)^n + n^2(R_0/\rho)^{2n}\right]. \quad (2.18)$$

The contribution to the force constant for a Born exponential repulsion, eqn (2.7), follows immediately from (2.18) when $m = 0$ and $n = 1$.

b. Electrostatic interactions

The interactions between the ion and the solvent dipoles and between the dipoles of the solvent themselves will have a constant representation in each of the potential energy functions. The inclusion or omission of induced dipolar interactions for the ion varies with the type of repulsion considered; the Lennard-Jones or Mie potentials, for example, implicitly include the induced dipolar interaction. Here, we consider a general form to be used throughout the disucssion in the next section.

From Böttcher[4] we can write the potential energy for the interaction between two *identical* dipoles of solvent as

$$\phi_{dd} = \frac{1}{\Lambda_1}\frac{\underset{\sim}{\mu}_1 \cdot \underset{\sim}{\mu}_2}{s^3} - \frac{3\Lambda_2}{\Lambda_1\Lambda_4}\frac{(\underset{\sim}{\mu}_1 \cdot \underset{\sim}{s})(\underset{\sim}{\mu}_2 \cdot \underset{\sim}{s})}{s^5}$$
$$- \frac{\alpha_s}{s^3}\left[\frac{1}{\Lambda_1}\frac{\underset{\sim}{\mu} \cdot \underset{\sim}{\mu}}{s^3} + \frac{3}{\Lambda_1\Lambda_4}\frac{(\underset{\sim}{\mu} \cdot \underset{\sim}{s})^2}{s^5}\right] \qquad (2.19)$$

in which

$$\Lambda_n = 1 - n\frac{\alpha_1\alpha_2}{s^6}(3/8)^3 \qquad (2.20)$$

and μ is the magnitude of the dipole moment. The polarizability of the solvent is α_s. Finally, s is the distance between the centres of gravity of the dipoles.

The contribution from the interaction between the ion and a dipole is

$$\phi_{id} = - \frac{1}{\Lambda_4}Ze\frac{(\underset{\sim}{\mu}_s \cdot \underset{\sim}{R})}{R^3} - \frac{\alpha_i}{2R^3}\left[\frac{1}{\Lambda_1}\frac{\underset{\sim}{\mu}_s \cdot \underset{\sim}{\mu}_s}{R^3} + \frac{3}{\Lambda_1\Lambda_4}\frac{(\underset{\sim}{\mu}_s \cdot \underset{\sim}{R})^2}{R^5}\right] - \frac{Ze^2\alpha_s}{2\Lambda_4 R^4} \ . \qquad (2.21)$$

in which R is the distance between the ion and the centre of gravity of the dipole. The polarizability of the ion is α_i. Now, in Λ_n, one of the polarizabilities is that of the ion and the other is that of the solvent, α_s.

It is not difficult to show that for the distances applicable to the solvated ionic species, the Λ_n all are essentially unity. In the following, we will use the simpler forms in which all $\Lambda_n = 1$.

The distance R between the ion and the dipole is the parameter of interest. Therefore, it is necessary to express the distance

s between the molecules of solvent in terms of R. For the regular tetrahedron and octahedron, this is a simple process. Furthermore, it is possible to relate the orientations of the dipoles to the unit vector $\hat{R}_i$ for the ith molecule. If we assume an orientation which yields the optimum interaction between the ion and the solvent dipole, then the dipole vectors can be written as

$$\underset{\sim}{\mu}_1 = \mu\hat{R}_1$$
$$\underset{\sim}{\mu}_2 = \mu\hat{R}_2$$

for a pair of dipoles, and

$$\underset{\sim}{s} = |\underset{\sim}{R}_1 - \underset{\sim}{R}_2|.$$

For any pair of dipoles,

$$\underset{\sim}{\mu}_1 \cdot \underset{\sim}{\mu}_2 = \mu^2\cos\theta$$
$$= \mu^2\hat{R}_1 \cdot \hat{R}_2,$$

and

$$\underset{\sim}{\mu}_1 \cdot \underset{\sim}{s} = \mu\hat{R}_1 \cdot (\underset{\sim}{R}_2 - \underset{\sim}{R}_1) = \mu R(\cos\theta - 1)$$
$$\underset{\sim}{\mu}_2 \cdot \underset{\sim}{s} = -\mu R(\cos\theta - 1).$$

In calculating the total contribution to the potential energy function due to the interactions between all the dipoles in a tetrahedron, we multiply the basic result for a single pair by 6 (i.e., $n(n-1)/2$ for n identical species). On the other hand, for the octahedron, we multiply the basic result by 12 (i.e., $n(n-1)/2$ -3 which eliminates the three pairs which are separated by the centrally located ion).

The specific forms for the dipole-dipole and ion-dipole energies are the following. For the four-coordinated tetrahedron,

$$^4\Phi_{dd} = 10(3/8)^{3/2}\frac{\mu^2}{R^3}[1 - (3/8)^{3/2}\alpha_s/R^3] \tag{2.22}$$

and

$$^{4}\Phi_{id} = -4\frac{Ze\mu}{R^2} - 2\frac{\alpha_s e^2}{R^4} - 8\frac{\alpha_i \mu^2}{R^6} \ . \tag{2.23}$$

For the six-coordinated octahedron,

$$^{6}\Phi_{dd} = \frac{3}{\sqrt{2}} \frac{\mu^2}{R^3}\left(3 - \frac{5}{2\sqrt{2}} \frac{\alpha_s}{R^3}\right) \tag{2.24}$$

and

$$^{6}\Phi_{id} = -6\frac{Ze\mu}{R^2} - 3\frac{\alpha_s e^2}{R^4} - 12\frac{\alpha_i \mu^2}{R^6} \tag{2.25}$$

c. The total potential energy

The total potential energy function is obtained by adding a repulsion to the sum of $^c\Phi_{dd}$ and $^c\Phi_{id}$. Thus, the total potential function is written as

$$^{c}U(R) = \ ^{c}\Phi_r + \ ^{c}\Phi_{dd} + \ ^{c}\Phi_{id}. \tag{2.26}$$

For some models, the repulsion is combined with a van der Waals attraction, as is the case for the Lennard-Jones potential. When it is clear that a van der Waals attraction between the ion and solvent is implicit in $^c\Phi_r$, then specific account of the interaction is omitted from eqn (2.23) and (2.26), (and hence in (2.26)), viz.,

$$2c\frac{\alpha_i \mu^2}{R^6}$$

is omitted.

Mechanical equilibrium is specified in terms of R_0, the
equilibrium value of the radius of solvation, by

$$U'(R_0) = 0. \tag{2.27}$$

Thus, we can write

$$c_{\phi'_{rep}} + 2\frac{e\mu}{R_0^3} + 2\frac{\alpha_s e^2}{R_0^5} + 12\frac{\alpha_i \mu^2}{R_0^7} + \frac{1}{c}(^c\phi_{dd})' = 0 \tag{2.28}$$

in which

$$(^4\phi_{dd})' = -30(3/8)^{3/2}\frac{\mu^2}{R_0^4}\left[1 - 2(3/8)^{3/2}\frac{\alpha_s}{R_0^3}\right] \tag{2.29}$$

or

$$(^6\phi_{dd})' = -\frac{9}{\sqrt{2}}\frac{\mu^2}{R_0^4}\left[3 - \frac{5}{\sqrt{2}}\frac{\alpha_s}{R_0^3}\right] \tag{2.30}$$

and

$$c_{\phi'_W} = -\frac{B}{R_0^{m+1}}\left[m + n(R_0/\rho)^n\right] \tag{2.31}$$

for the Woodcock generalized exponential repulsion.

Eqn (2.28) yields an equation in the adjustable parameters.
The complete expression for the force constant yields another equation.
Thus, with the assumption of the value of the solvation radius
at equilibrium and the value of the force constant for the far
infrared-active vibrations, it is possible to determine the

values of the adjustable parameters for a particular ion. This
process is carried out in the next section.

3. Analyses with specific functional forms

The analyses to be considered conviently divide into those
which depend upon exponential forms for the repulsion, and those
which depend upon inverse powers.

I. Exponential forms

The simple Born exponential repulsion is contained as a
limit in the Woodcock generalized exponential repulsion. Thus,
to begin, we consider the Woodcock form.

Following the prescription laid down in the last section,
we proceed here to determine the values of the adjustable parameters.
From the equilibrium condition, eqn (2.28), we can write the
following

$$B(m + nx) = R_0^{m+1}\left[2\frac{e\mu}{R_0^3} + 2\frac{\alpha_s e^2}{R_0^5} + 12\frac{\alpha_i \mu^2}{R_0^7} + \frac{1}{c}(^c\phi_{dd})'\right]$$

$$= P_c \tag{3.1}$$

in which we have defined x as

$$x = (R_0/\rho)^n. \tag{3.2}$$

The expression for the force constant can be expressed as

$$B[m(m-1) - n(n-2m+1)x + n^2x^2]$$

$$= 3R_0^{m+2}\left[\frac{1}{c}k + 2\frac{\alpha_s e^2}{R_0^6} + 20\frac{\alpha_i \mu^2}{R_0^8}\right]$$

$$= Q_c. \tag{3.3}$$

These two equations can be solved for B and x. The elimination of B yields

$$x = \frac{(n-2m+1)P_c + Q_c}{2nP_c} \pm \frac{1}{2nP_c}\left\{[n^2+2n-4mn-4m+5]P_c^2 + 2(n+1)P_cQ_c\right.$$
$$\left. + Q_c^2\right\}^{1/2} \tag{3.4}$$

The value of ρ is

$$\rho = R_0/x^{1/n}. \tag{3.5}$$

Finally, the value of B is found to be

$$B = P_c/(m + nx). \tag{3.6}$$

The Born repulsion follows from the Woodcock form with $m = 0$ and $n = 1$. Values of B and ρ for the Born potential are given in Table 2.

Woodcock,[4a] in studying the alkali halides, assumed a value of $m=4$. The value of n ranged from 1 to 6. We assume values of $m = 4$ and $n = 6$. The results, values of B and ρ for the solvated alkali cations, are given in Table 3.

II. Inverse powers

Up to this point we have used forms for the potential which depend upon two parameters within the repulsion. It is useful and instructive to shift attention from these exponential forms in order to consider another common form of interaction, the R^{-12} repulsion. When this form of repulsion is combined with an R^{-6} attraction as

$$\phi_M = A/R^{12} - B/R^6 \tag{3.7}$$

we have an example of the Mie potential.[12] On the other hand, these two terms can be combined as

$$\phi_{LJ} = 4D[(\sigma/R)^{12} - (\sigma/R)^6] \tag{3.8}$$

which is a Lennard-Jones potential.[13] The quantity σ is a distance for which the potential vanishes. For our purposes, it is more convenient to use (3.8) in the form

$$\phi_{LJ} = \varepsilon(\rho/R)^6[(\rho/R)^6 - 2] \tag{3.9}$$

$$\varepsilon = -D.$$

When eqn (3.7) or (3.9) is combined with other terms to give a potential of the form

$$^cU(R) = - c\frac{Ze\mu}{R^2} - c\frac{\alpha_s e^2}{2R^4} + {}^c\phi_{dd} + \phi_{(M \text{ or } LJ)} \tag{3.10}$$

the quantities A and B or ε and ρ are parameters which are to be determined with the use of the experimental data.

To begin, we examine the use of (3.10) with the Lennard-Jones component. This form of potential is analogous to the Stockmayer form of hybrid potential which is used in the analysis of polar molecules.[14] As we illustrate momentarily, the use of this form of potential with the values of the quantities R_0, α_s, and μ in Table 1 leads to a mathematical pathology; an intrinsically positive definite quantity is determined to be negative.

The complete force constant for the potential with a Lennard-Jones component is

$$k = 4c\frac{\epsilon}{R_0^2} (\rho/R_0)^6[11(\rho/R_0)^6 - 5] - 2c\frac{\alpha_s e^2}{R_0^6} . \qquad (3.11)$$

Define the quantity x as

$$x = (\rho/R_0)^6 . \qquad (3.12)$$

Then, with the use of $U'(R_0) = 0$, we find

$$\epsilon x(x - 1) = A$$
$$\epsilon x(11x - 5) = B \qquad (3.13)$$

with

$$A = \frac{Ze\mu}{6R_0^2} + \frac{\alpha_s e^2}{6R_0^4} + \frac{R_0}{12c} (^c\Phi_{dd})' \qquad (3.14)$$

and

$$B = \frac{1}{4c} R_0^2 k + \frac{\alpha_s e^2}{2R_0^4} . \qquad (3.15)$$

The pair of equations (3.13) are solved easily for x and ϵ:

$$x = \frac{5A - B}{11A - B} \qquad (3.16)$$

Here, the pathology appears. For lithium, or any of the cations of group 1, we find $x < 0$. By definition, however, eqn (3.12), x must be greater than zero. Hence, the contradiction suggests either (1) the use of the Lennard-Jones component is inappropriate or (2) the values of R_0 used are inappropriate. We return to consider this question briefly in the next section.

The Mie potential is a decoupled form of Lennard-Jones potential. The adjustable parameters A and B can be determined easily as follows. The complete force constant is

$$k = 2c\left(22\frac{A}{R_0^{14}} - 5\frac{B}{R_0^8} - \frac{\alpha_s e^2}{R_0^6}\right). \qquad (3.17)$$

Let

$$a = A/R_0^{12}$$
$$b = B/R_0^6 \qquad (3.18)$$

Then, we find the equations

$$6a - 3b = X$$
$$22a - 5b = Y \qquad (3.19)$$

with

$$X = \frac{2e\mu}{R_0^2} + \frac{\alpha_s e^2}{R_0^4} + \frac{R_0}{2c}(^c\phi_{dd})' \qquad (3.20)$$

and

$$Y = \frac{1}{2c}R_0^2 k + \frac{\alpha_s e^2}{R_0^4} \qquad (5.21)$$

Thus,

$$a = \frac{1}{12}(Y - 5X/3)$$

$$\qquad (5.22)$$

$$b = \frac{1}{6}(Y - 11X/3).$$

The results of the application of these equations to the alkali metal cations are given in Table 4. It is remarkable to note that for both lithium and sodium, the value of B found is *negative*. Thus, for both of these ions we find an R^{-6} *repulsion* in addition to the R^{-12} repulsion when $c = 4$.

4. Discussion

For some time now, the problem of the determination of the energies of solvation has commanded much attention.[15-17] These efforts amply show that electrostatic contributions predominate. Some calculations have been carried out which incorporate an accounting for repulsive interactions.[16,17] As one expects, the repulsion is only a small contribution to the total energy of solvation. Thus, one would anticipate a lack of enthusiasm for the pursuit of the most accurate form of the repulsion, if the goal were only to determine the energies of solvation.

As we have shown, certain phenomena, principally the far infra- red spectra, depend sensitively upon the repulsion. In this paper we also have shown that these vibrations depend substantially upon

van der Waals and induced dipolar attractions which operate between the ion and the molecules of solvent. The energies of solvation are thermodynamic quantities which are characteristic of a state of equilibrium. On the other hand, the vibrational spectra of the solvated ions reflect the importance of terms in the potential energy function which influence time-dependent phenomena. Thus, although the repulsion and the induced dipolar and van der Waals interactions may play smaller roles in the determination of the energy of solvation, their role can become much enhanced for rate and transport processes.

It is possible, of course, to generate many different forms for the repulsion in the total potential. In the absence of any other measurable quantity, there is little upon which to base a choice of one form over another. Even though the repulsion and van der Waals attraction contribute but a fraction to the total energy of solvation, the magnitude of the contribution for one form as compared to another can be diagnostic.

In the previous section we considered three model potential energy functions in which only the repulsion contained adjustable parameters. In contrast, for the Mie potential, we determined coefficients for both the repulsion and the van der Waals terms. Thus, it is necessary to compare only functions which have the same overall form.

Table 5 lists the values of the repulsions and the Mie potential evaluated with the equilibrium radius of solvation. The Born and Woodcock terms all can be compared one to another.

It is clear that there is little to distinguish the Born from the Woodcock 4/6 potentials for the ions lithium, sodium and potassium.

The Born repulsion decreases monotonically. This is true also for the Woodcock potential. However, for the Woodcock 4/6 potential we see that changing from 4- to 6-coordination at Rb shows a dramatic change in the repulsion. This change is not true of the Born potential. As Muirhead-Gould and Laidler[17] have shown, there is a distinct difference in the trend in the energies of solvation upon changing from 4- to 6-coordination. This trend is matched by the experimental points. However, it is difficult to say at this point whether the trend depends significantly upon changes in the repulsion or not.

The Mie potential deserves special attention. First of all, the parameters A and B apply respectively to a formal repulsion and an attraction which operates between the ion and the molecules of solvent. In contrast, in the other models of the potential function, all the adjustable parameters apply to one part of the complete function, the repulsion. The use of the Mie potential, therefore, suggests that the representation is more physically "truthful" than is the case for the other more restricted models. There is no compelling reason to expect that the experimentally measured (or more accurately, estimated[5]) polarizabilities for the ions should apply to the van der Waals interaction between the ion and the solvent. The results with the use of the Mie potential seem to indicate that the experimental polarizabilities of the ions--as used for example with the exponential forms in section 3, part I-- may indeed not apply.

The values for the contribution of the Mie potential to the
total energy of solvation are listed in Table 5. These values
represent the combination of the repulsion and the attraction.
It is clear that the total effect of both terms is a net repulsion
at the equilibrium radius of solvation. The fact that there is a
trend downward from lithium to sodium and back upward from sodium
to caesium is accounted for by referring to the changing role of
the R^{-6} term as shown in Table 4. The ionic polarizabilities are
given in Table 1. For lithium and sodium, these quantities are
small. Thus, any induced dipolar, van der Waals attraction between
the ion and a molecule of solvent will be extremely small. For
example, for lithium we calculate this contribution to be 77 J mole^{-1}.
It would come as no surprise therefore to find small, but positive,
values of B for lithium and sodium. It is somewhat surprising to
find in fact that the polarizability has vanished (in terms of this
model) and that the van der Waals attraction is replaced by a
repulsion. Quantum mechanical calculations[18] to determine the
nature of the interaction between the lithium cation and the
formaldehyde molecule indicated that the lithium cation does not
participate in any covalent delocalization of electrons in either
the 1s or 2s shells. That work[18] concluded that lithium behaves
essentially as a hard, charged sphere. In light of this finding,
the role reversal of the R^{-6} term looses its surprisal value.
Lithium, and to a much lesser degree sodium, is simply a very
classical, charged particle.

It is of interest to see if there is any observable relation-

ship between the values for the B-factors which are determined by
matching the potential to the experimental quantities and the values
of the polarizabilities (listed in Table 1). We have seen above
that for lithium and sodium there can be no correspondence. The
fact that a negative value of B is found both for lithium and
sodium cannot support any interpretation which involves the
polarizability of the ion (viz., a van der Waals type of inter-
action). For the ions of potassium, rubidium, and caesium we find
positive values for the B-quantities, as given in Table 4.

At first glance, it does appear that there is some correspondence
between the B-values and the experimental values of the polariza-
bilities. We can assume that B is related to the polarizability
of the ion and the dipole moment of the solvent by[4]

$$B = f\alpha_i \mu^2. \tag{4.1}$$

The quantity f is a constant of proportionality. Table 6 lists
the values of $f\alpha_i$ with $f = 1$. All the values listed are very
large, much larger than the experimental polarizabilities. If we
assume that these values are large because f should not be unity, then
a constant value of f should emerge when we examine the ratio
$\alpha_{i(calc)}/\alpha_{i(exp)}$. These ratios are also included in Table 6. As is
readily seen, there is no consistancy. Lastly, we list the values
of $\alpha_{i(n)}/\alpha_{i(n-1)}$ for both the calculated and the experimental
quantities. There is no similarity here either.

We conclude that for the Mie potential at least, there is the
indication that the trends in the polarizabilities of the ions
are roughly followed. However, because the effective polarizabilities

are much larger than the experimental quantities, there appear to
be operating additional quantal effects [which would involve
electronic overlap] which are not adequately accounted for in terms
of the simplicity of the potential energy functions used.

The results obtained for the Mie potential suggest that the
pathology observed with the use of the Lennard-Jones component is
intrinsically associated with the form and not with the values of
the parameters used. The Lennard-Jones potential, when used by
itself, adequately represents the balance between attraction and
repulsion with two parameters, an energy and a distance. When used
in conjunction with a strong interaction such as an electrostatic
ionic-dipolar interaction, it may not be possible for the parameters
rationally to adjust in a physically reasonable sense. Thus, we
suspect that it is more appropriate to use forms for the potential
which consist of independently variable repulsions and attractions.

We cannot claim to have unearthed the accurate form of the
potential energy function which operates to describe ionic solvation.
However, we claim to have accented some factors which have
received less attention than they warrant, namely, the roles played
by the repulsion and dispersion forces. The question must therefore
be, what is the accurate form of the potential. A considerable
body of work in related areas[19,20] suggests that accurate potential
energy functions can be constructed in terms of individual atomic
and electronic (bonding and lone pair) contributions from all the
atoms in the molecular aggregate. Scheraga's efforts,[19] in particular,
have been notably successful in a programme to parameterize a
large number of interactions. A feature of Scheraga's work which
seems also to be applicable to the solvated ion is the use of a

three-parameter potential for each "electron". The electrons in
Scheraga's model are negative point charges which are not
necessarily located at the same positions as the actual quantal
electronic charge distributions. The potential Scheraga[19] uses for
the interaction between electrons is the Buckingham exp-6 form.
Dispersive interactions are associated only with the electrons.
The parameters are then fixed by means of least squares fits to all
avaliable experimental data and to some quantum mechanical calcula-
tions in regions where strong repulsions operate.

Unless one is content to use the R^{-12} or similar form of
repulsion in the potential energy, then the use of an exponential
form for the repulsion requires two adjustable parameters.
As we have seen with the Mie potential, it is useful to be able
to determine the coefficient of the van der Waals term by fitting
to experimental data as well. Thus, to be able to fit both the
repulsions and the dispersive forces requires a minimum of three
adjustable parameters.

The use of the exponential form for the repulsion has a long
tradition. And, its use seems to be more closely related to actual
quantum mechanically calculated repulsions than is the case for the
R^{-12} repulsion.[22] Thus, we suspect that the accurate form of the
potential energy function for a solvated ionic system which will
emerge will be one which faithfully reproduces the vibrational
spectra of the ion in the cage of solvent, and the cage itself.
Moreover, the function ought to be able to predict vibrational
contributions to the activation of rate and transport processes.
It seems at this time that a hybrid form which uses the exponential
repulsion together with the van der Waals attraction for part of

the potential will be successful .

Acknowledgment

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Table 1: Experimental data for use in determining potential energy functions

Solvent: dimethyl sulphoxide: $n = 1.4783$ (Na D-line), $\mu = 4.3$ debye

$$\alpha = 8\overset{\circ}{A}{}^3 \text{ (a)}$$

Ion	$R_0(\overset{\circ}{A})$	$\nu(cm^{-1})$ [b]	$k(dyn\ cm^{-1})$ [c]		$\alpha_i(\overset{\circ}{A}{}^3)$ [d]
			4-coord	6-coord	
Li^+	3.24	429±2	74307	74894	0.08
Na^+	3.56	198±3	49497	50652	0.20
K^+	3.79	153±3	47837	49672	0.87
Rb^+	3.91	123±3	60121	64785	1.43
Cs^+	4.12	110±4	66506	73888	2.50

(a) Refractive index and dipole moment: Merck Index (Merck Publishing Co., Raway N.J., 1976); polarizability from refractive index and eqn (2.6).

(b) From Maxey and Popov, see ref. 2

(c) Calculated from Maxey and Popov's data[2] for 4- and 6-coordination, see ref. 1.

(d) From Smyth, ref. 6.

Table 2: Model potential with Born exponential repulsion

Ion	$B \times 10^{12}$ erg		$\rho \times 10^8$ cm	
	4-coord	6-coord	4-coord	6-coord
Li^+	0.51	0.59	0.26	0.32
Na^+	0.38	0.43	0.27	0.34
K^+	0.27	0.30	0.24	0.30
Rb^+	0.18	0.20	0.18	0.22
Cs^+	0.12	0.13	0.15	0.17

Table 3: Model potential with Woodcock 4/6 exponential repulsion

Ion	$B \times 10^{44}$ erg-cm^4		$\rho \times 10^8$ cm	
	4-coord	6-coord	4-coord	6-coord
Li^+	59.57	176.53	3.02	3.58
Na^+	63.18	186.91	3.29	3.67
K^+	59.38	172.41	3.24	3.77
Rb^+	49.16	142.05	3.40	3.72
Cs^+	42.62	122.40	3.46	3.77

Table 4: Model potential with Mie components

Ion	$A \times 10^{102}$ erg cm^{12}		$B \times 10^{58}$ erg cm^6	
	4-coord	6-coord	4-coord	6-coord
Li$^+$	0.68	0.49	-0.75	-0.56
Na$^+$	0.69	1.23	-0.01	0.56
K$^+$	4.43	3.20	9.57	6.99
Rb$^+$	9.71	7.22	31.88	24.22
Cs$^+$	23.96	18.20	71.23	55.25

Table 5: Differences in ϕ_{rep} as a contribution to the free energy/of cationic solvation

kJ mole^{-1}

Ion	Born	Woodcock	Mie
Li$^+$	30.71	32.55	30.88
Na$^+$	22.89	23.68	10.04
K$^+$	16.28	17.91	29.04
Rb$^+$	12.06	36.61	31.21
Cs$^+$	7.82	25.61	41.09

Table 6: Effective polarizabilities from $B = \alpha_i \mu^2$

Ion	$\alpha_{i(calc)}$ ($\mathring{A}^3$)	$\alpha_{i(n)}/\alpha_{i(n-1)}$ [a]	$\alpha_{calc}/\alpha_{exp}$
K^+	52		60
		2.52(1.64)	
Rb^+	131		92
		2.28(1.75)	
Cs^+	299		120

(a) Parenthetic values are listed for the experimental quantities. Here, n refers to the identity of the ion in the sense of increasing atomic number.

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